



CNCS



# **POLYROTAXANES BASED ON $\pi$ - CONJUGATED BACKBONE FOR MICRO/OPTOELECTRONIC APPLICATIONS**

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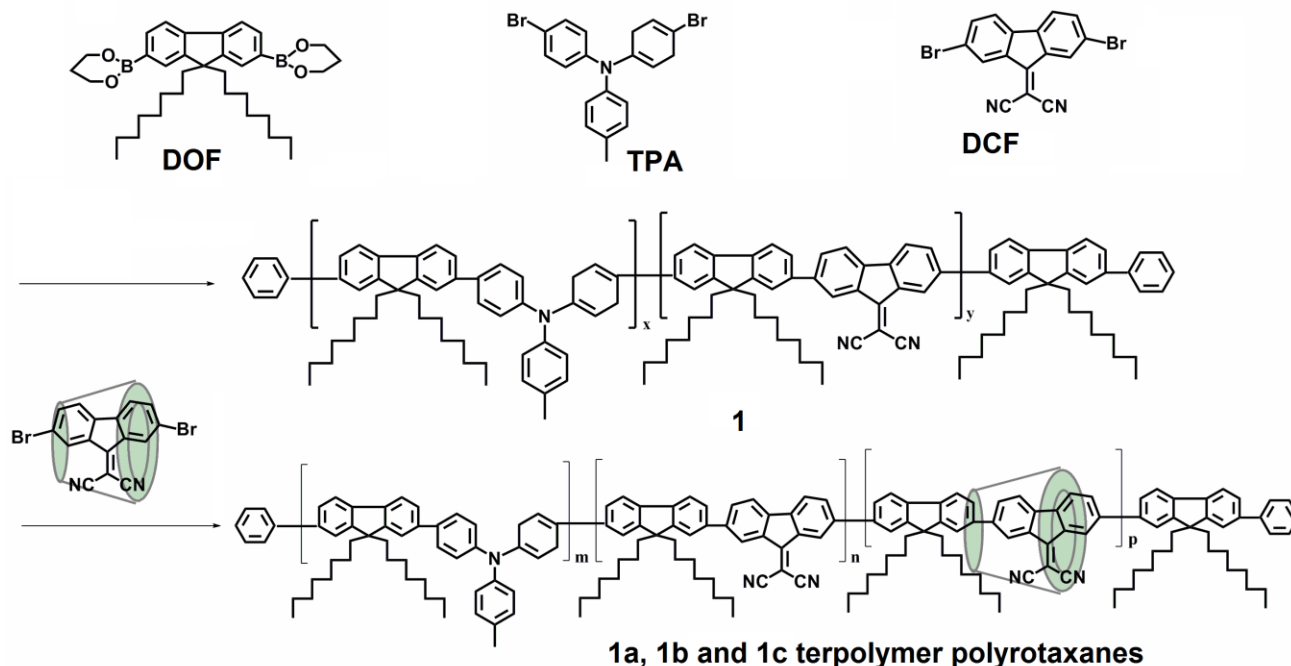
# ABSTRACT

Although conjugated polymers (CPs) are very promising light emitting materials, their use is often affected by several limitations including undesirable intermolecular interactions in the solid state, which leads to lower quantum yield (PL) as result of the fluorescence quenching effects. In this process the characteristic blue emission disappears and a red shift or even green emission appears due to the irreversible changes in the polymer backbones. Different strategies have been employed with a view to reduce these undesirable effects. Among the wide variety of strategies, the construction of conjugated polyrotaxanes have attracted considerable attention because these supramolecular architectures offer a great opportunity to suppress the intermolecular interactions of the conjugated backbones. Likewise, it was demonstrated that the aggregation tendency of CPs and the fluorescence quenching effects in the solid states can be diminished by encapsulating the  $\pi$ -conjugated backbones into a macrocyclic cavity. In addition, the presence of macrocycles in polyrotaxane architectures could effectively increase distances between the conjugated backbones and open the possibility of improving the physico-chemical properties of CPs. The majorities of reported conjugated polyrotaxanes have showed distinct improvements in solubility, molecular weight, film forming ability, improvement of molecular rigidity and optimize optical and electronic properties.

In this work we studied the optical, electrochemical behaviors, wetting and surface free-energies, as well as the morphological properties of CPs with electron-rich (D) and electron-deficient (A) groups statically distributed into polyfluorene (PF) backbones and PF polyrotaxanes with 2,3,6-tri-O-trimethylsilyl cyclodextrins (TMS-CD).

## OBJECTIVES - 2016

### **1. Electro-optical characteristics of polyfluorene with randomly distributed electron-donor and rotaxane electron-acceptor units**



**FIGURE 1.** Chemical structures of the neat copolymer **1** and **1a**, **1b** and **1c** polyrotaxanes.

In our study, the encapsulation of 9,9-(dicyanomethylene) fluorene (DCF) units into macrocycle cavities was employed with a view to diminish cyano groups quenching effects by solvent, impurities or oxygen molecules. The first step in the preparation of these copolymers is the threading of  $\gamma$ -CD, TMS- $\beta$ CD or TMS- $\gamma$ CD macrocyclic molecules onto DCF (as A units). By reacting DOF (as bulky group) with 4,4'-dibromo-4''-methyl-triphenylamine (TPA) (as D units) and DCF encapsulated into  $\gamma$ -CD, TMS- $\beta$ -CD or TMS- $\gamma$ -CD in a 5:4:1 molar ratio, followed by the termination of the growing chains with bromobenzene, **1a**, **1b** and **1c** polyrotaxanes were obtained, Fig. 1.

## The optical properties of the investigated compounds

The influence of the host nature on the optical properties was investigated by UV-Vis and PL measurements in THF solution or in solid state. The results for the absorption in solid state of polyrotaxanes revealed a strong absorption at about 380, 383 and 385 nm, which can be assigned to the  $\pi$ - $\pi^*$  transition derived from the conjugated fluorene backbones, Table 1.

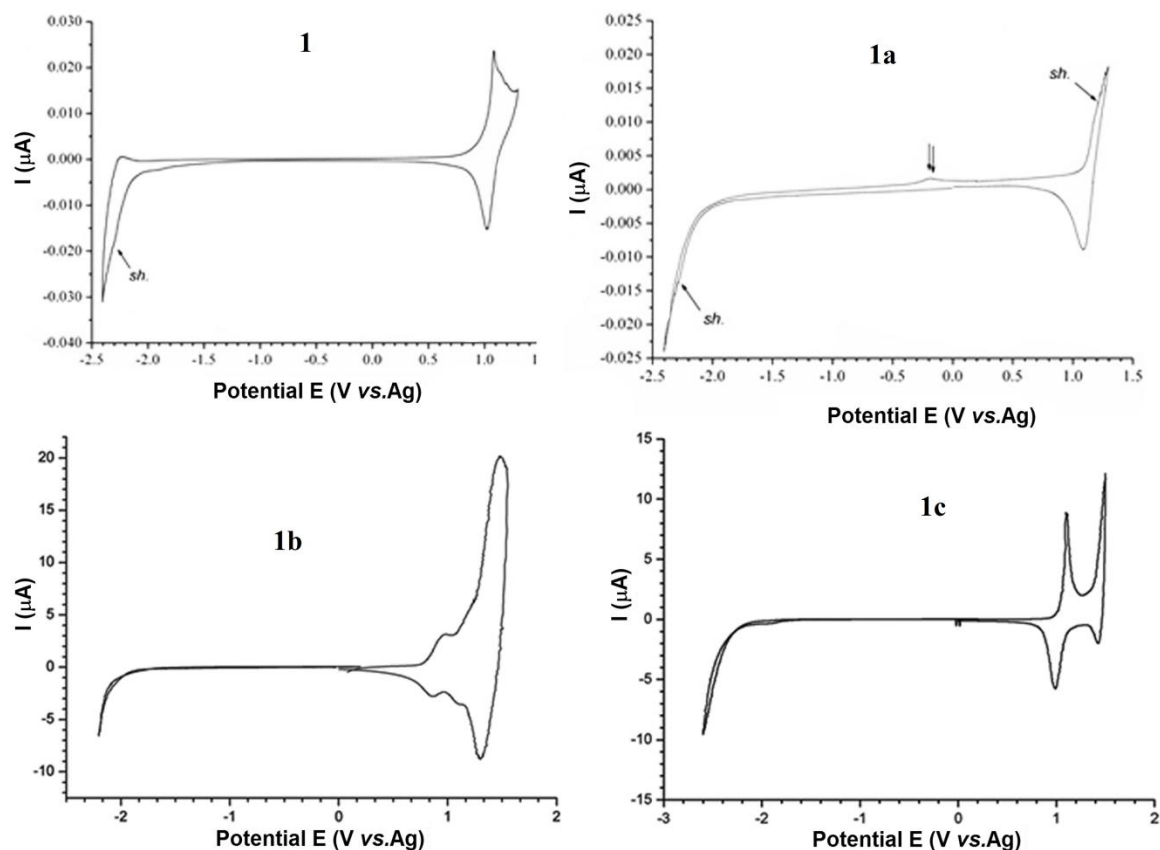
**Table 1.** Optical properties of the investigated compounds

Sample	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	$\Phi_{PL}$ (%)	$\tau_1$ (ns)	$\tau_2$ (ns)	$\Delta E_g$ (eV)
<b>1</b>	383	418, 531	7.0	0.88	1.56	2.98
<b>1a</b>	380	437	19.0	-	-	2.94
<b>1b</b>	385	418, 530	17.6	1.03	-	2.88
<b>1c</b>	383	419, 527	16.3	1.14	-	2.90

The decay traces of the reference **1** obtained from the  $\tau_F$  measurements follows a bi-exponential decay consisting of a main component with a relative short time of  $\tau_1=0.88$  (57.08 %) and a minor component with a longer lifetime of  $\tau_2=1.56$  ns (42.92 %), Table 1. The observed behavior would suggest that the bi-exponential decay of the non-rotaxane **1** can be associated to the intrachain emission and excitonic lifetime, whereas in the polyrotaxanes only to the excitonic contribution.

## Electrochemical properties

CVs of these investigated compounds are shown in Figure 2. CV scans of the samples exhibit the oxidation and reduction processes. From their onset potentials, it was possible to estimate precisely the values of HOMO (IP), LUMO (EA) and  $\Delta E_g$ . The observed CVs behaviors suggest that the encapsulation of DCF moieties results in a smaller electrochemical  $\Delta E_g$ , HOMO, as well as LUMO than that of the non-rotaxane counterpart.

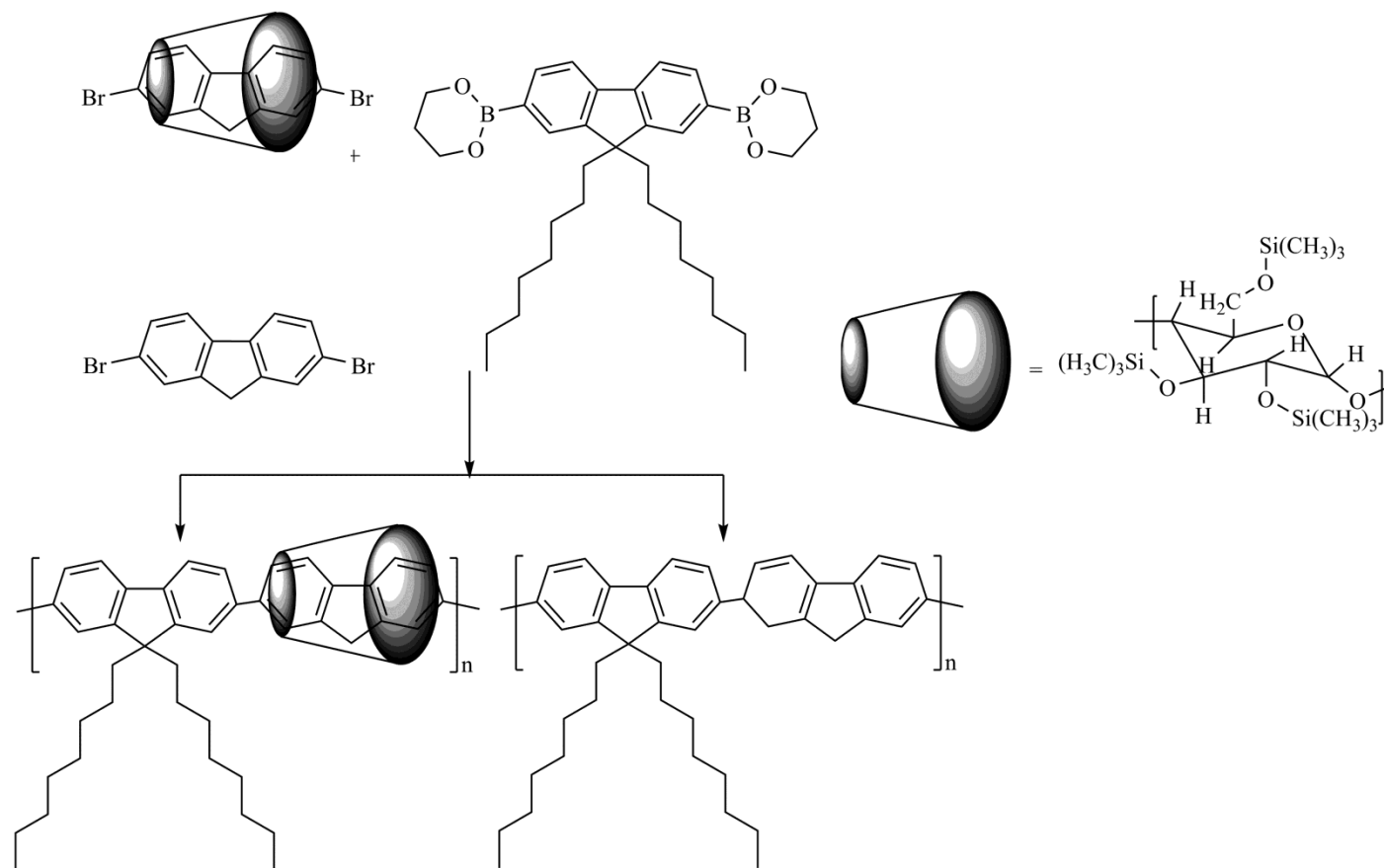


**FIGURE 2.** CV of the investigated polymeric films coated on Pt plate electrodes in 0.1 M TBAPF<sub>6</sub>/ACN solution at a scan rate of 20 mV·s<sup>-1</sup>

## Application to OLED and photovoltaic device fabrication

The HOMO/LUMO energy levels of the unthreaded polymer **1** and its corresponding **1a** polyrotaxane in combination with the electronic potentials of the anodic indium tin oxide (ITO) glass substrate (-4.75 eV) and cathodic aluminum (-2.2 eV), prove that the required energy level is fulfilled for fabrication of organic light-emitting diodes (OLEDs). The HOMO/LUMO energy levels of **1b** and **1c** in combination with the work function of anodic ITO glass substrates coated with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (-5.2 eV) and cathodic Ca (-2.8 eV) or Al (-2.2 eV) indicate that they are also electrochemically accessible as electron-transporting materials. The relative position of the frontier energy levels of such architectures may also be advantageous to photovoltaic (PV) applications. Furthermore, these results suggest that the polyrotaxanes could be useful for the fabrication of diffuse heterojunctions between interpenetrating networks of *n*- and *p*-type semiconductors. In addition, the encapsulation of the conjugated polymer units into TMS- $\beta$ CD or TMS- $\gamma$ CD cavities leads to distinct improvements of solubility of resulting polyrotaxanes in common organic solvents (e.g., THF, DCM, CHCl<sub>3</sub> or toluene) with respect to **1a**, which is soluble in THF/DMF = 3/1 v/v. Also, with encapsulation of per-TMS modified CDs, the transparency of solid films has been improved along with the increased molecular weights and glass-transition temperatures. Overall, the HOMO/LUMO energy levels of studied polyrotaxanes proved that these polyrotaxane structures, as well as their references are electrochemically accessible as electron-transporting materials.

## 2. Synthesis of polyfluorenes with persilylated $\beta$ - and $\gamma$ -cyclodextrin main-chain polyrotaxanes



**SCHEME 1.** Synthesis of polyfluorenes/persilylated  $\beta$ - and  $\gamma$ -cyclodextrin main-chain polyrotaxanes

TMS-CD encapsulation of PFs backbones leads to distinct improvements in the solubility, molecular weights, film forming ability and thermal stability. The optical investigations confirmed that the polyrotaxanes exhibited higher fluorescence quantum yield and fluorescence lifetimes.



## Synthesis and photophysical characteristics of polyfluorene polyrotaxanes

Polyfluorenes/persilylated  $\beta$ - and  $\gamma$ -cyclodextrin main-chain polyrotaxanes have been synthesized through the Suzuki cross-coupling reaction of 2,7-dibromofluorene encapsulated into TMS- $\beta$ CD, TMS- $\gamma$ CD or CB7 cavities and 9,9-dioctylfluorene as bulky stopper units, Scheme 1. In this approach a small excess of 9,9-dioctylfluorene was added at the end of polymerization to introduce ester groups at both polymer chain ends, and finally bromobenzene was added as a monofunctional end-capping reagent to react with the boronic ester end groups. Thus, a copolymer having stable phenyl groups at both ends was obtained. The spatial distribution of octyl groups is larger enough than the diameter of the inner cavities of TMS- $\beta$ CD, TMS- $\gamma$ CD or CB7 indicating their blocking effect. Encapsulation of 2,7-dibromofluorene units into macrocycle cavities has been used to protect its 9 position against oxidative degradation.  $^1\text{H}$  NMR spectroscopy provides a low coverage value for the polyrotaxane derived from TMS- $\gamma$ CD compared to those obtained from TMS- $\beta$ CD. The formation of PF polyrotaxanes also was confirmed by SEC analysis, where no free macrocycle peaks was present in the chromatogram, which clearly denoted that the polyrotaxane samples are not a physical mixture between components. The chromatogram of polyrotaxanes is situated at lower elution volumes as compared to that corresponding to the non-threaded copolymers, evidencing their higher molecular weights. The presence of TMS- $\beta$ CD or TMS- $\gamma$ CD onto PF backbones increase the thermal stability of main-chain polyrotaxanes and improves their solubility in halogenated solvents.

## Photophysical properties of polyfluorene polyrotaxanes

The UV-Vis absorption spectra of the non-rotaxane shows a featureless band peaking at 374 nm. Upon encapsulation with the TMS- $\beta$ CD, a hypsochromic shift of about 7 nm attributed to a reduction of intermolecular interactions and/or a variation of the polarity, when the PF core is inside the macrocycles cavity is identified. The PL emission of the non-rotaxane copolymer shows three vibronic components at about 418, 435 and 460 nm. The intensity of the 0-1 PL band (435 nm) for diluted  $\text{CHCl}_3$  solution is the most intense. At the same concentration, PF polyrotaxane with TMS- $\beta$ CD exhibited a slight blue-shift (2 nm) of the emission. The ratio of the emission intensity of the 0-0 transition for this polyrotaxane is higher than that of the 0-1 transition, contrary to what we observe for the non-rotaxane counterpart. Such trends suggest that the encapsulation with TMS- $\beta$ CD acts to reduce intermolecular interactions, in agreement with previous reported results. It appears that TMS- $\beta$ CD is much more effective than TMS- $\gamma$ CD for suppressing intermolecular interactions upon an increase of the polymer concentration. The temporal decays of  $10^{-3} \text{ mg}\cdot\text{mL}^{-1}$  in  $\text{CHCl}_3$  solutions of the polyrotaxane with TMS- $\beta$ CD and the reference are mono-exponential with a  $\tau_F$  of  $\sim 0.6$  ns, whereas the polyrotaxane with TMS- $\gamma$ CD shows a bi-exponential decay consisting of a main component with  $\tau_{F1} = 0.7$  ns (98%) and a minor component with a longer  $\tau_{F2} = 5.4$  ns (2%). The longer  $\tau_F$  for the polyrotaxane with is TMS- $\gamma$ CD, consistent with interchain states and they are plausible, considering the significantly bigger size of the  $\gamma$ CD, which might favor both unthreading of the cores, or even accommodation of more than one core unit within the macrocycles cavities. The HOMO/LUMO energy levels of these polyrotaxane copolymers imply that all copolymers are electrochemically accessible as electron-transporting materials.

## Cucurbit[7]uril based fluorene polyrotaxanes

Poly[2,7-(9,9-dioctylfluorene)-*alt*-(2,7-fluorene/cucurbit[7]uril)] polyrotaxane was synthesized according to Suzuki coupling protocol in DMSO, by reacting 2,7-dibromofluorene encapsulated into the cucurbit[7]uril (CB7) cavity with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The  $K_a$  value ( $9.5 \times 10^3 \text{ M}^{-1}$ ) indicates that 2,7-dibromofluorene provides a preferential binding to CB7, which allows the synthesis of a polyrotaxane with CB7/structural unit ratio of about 1/3 and higher molecular weights. The chemical structure was proved by FTIR and  $^1\text{H}$ -NMR spectroscopy. The resulting polyrotaxane with CB7 contains 27.4% coverage (quantified by  $^1\text{H}$ -NMR), but some error is expected due to its low solubility in DMSO- $\text{d}_6$ . Note that DMSO- $\text{d}_6$  it is not a good solvent for PFs chains and that only CB7 induces polyrotaxane's solubility. The  $^1\text{H}$ -NMR in DMSO- $\text{d}_6$  shows characteristic peaks for both PFs chains and CB7, but the signals are not very well resolved. The thermal, optical, electrochemical, wetting and surface morphological properties of the polyrotaxane have been investigated and compared to those of the neat copolymer. The polyrotaxane exhibits an enhancement in the glass transition temperature, blue-shifts absorption of about 11 nm and a subtle effect on the LUMO energy levels. The fluorescence lifetime follow a mono-exponential decay with a value of  $\tau_F = 0.7 \text{ ns}$ . The electrochemical band gap of the polyrotaxane (3.39 eV) is smaller than that of the neat compound. The comparison of the HOMO/LUMO energy levels of the polyrotaxane and the corresponding non-rotaxane with the electronic potentials of the anodic indium tin oxide (ITO) glass substrate (-4.75 eV) and cathodic aluminum (-2.2 eV) reveals that the required energy level criteria for the fabrication of organic light-emitting diodes (OLEDs) are nicely met.

## Future prospects

Despite the advances made by these preliminary investigations, additional information on energy levels of charge carriers in terms of polyfluorene polyrotaxanes in solid states, the nature of electrolyte and solvent, and electrodes in electrochemical doping/dedoping processes require further exploration. The broad range of properties outlined here can be tuned by straightforward structural modifications designed to make them suitable alternate replacements for the non-rotaxane counterparts, especially if one takes into account of their good fluorescence efficiency, surface morphology, high oxidative and chemical stability, and quenching strength. The macrocyclic encapsulations by various classes of macrocyclic molecules suppress the tendency of aggregate formations by diminishing intermolecular interactions of PF backbones. The properties of PF polyrotaxanes can be readily optimized by incorporation of various host molecules, such as CB7. The presence of CB7 results in improved solubility in water, which allows their processing by spin-coating. Development of new polyrotaxane architectures should be beneficial, especially in the field of materials for the generation of active layer in organic electronic devices, such as organic light emitting diode (OLED) and photovoltaic (PV) devices. These findings are relevant to their applications in OLED, where it is essential to prevent luminescence quenching without hindering charge transport. It is believed that further research into conjugated polyrotaxanes for organic electronics will continue to furnish excellent achievements in succession to the rapid progress. Despite the interest in synthetic approaches, the interdisciplinary collaborations serve to continue a high level of interest for the generation of active layer in organic electronic devices.

## Results 2016

### A. Published Papers in ISI Journals

1. A. Farcas, *Cyclodextrins in rotaxa-conjugated polymers synthesis*, *Cellul. Chem. Technol.*, 50 (5-6), 585-591 (2016)
2. A. Farcas, K. I. Assaf, A.-M. Resmerita, S. Cantin, M. Balan, P.-H. Aubert, W. M. Nau, *Cucurbit[7]uril based fluorene polyrotaxanes*, *Eur. Polym. J.*, 83, 256-264 (2016)
3. A. Farcas, A.-M. Resmerita, F. Farcas, *Terpolymer polyrotaxanes: a promising supramolecular system as electron-transporting materials for optoelectronics*, accepted for publication in [Proceedings of SPIE-The International Society for Optical Engineering](#), decembrie-2016
4. A.-M. Resmerita, F. Farcas, A. Rotaru, A. Farcas, *Synthesis and photophysics of conjugated azomethine polyrotaxanes*, accepted for publication in [Proceedings of SPIE-The International Society for Optical Engineering](#), decembrie-2016
5. V. Malov, A. Tameev, S. Kostromin, S. Bronnikov, A. Farcas, *Photovoltaic effect and charge transfers mobility in the layers of compositions containing bithiophene copolymer/bithiophene based rotaxane and fullerene C70 derivative*, *Tech. Phys. Lett.*, accepted September 2016
6. A.-M. Resmerita, F. Farcas, P.-H. Aubert, A. Farcas, *Conjugated polyrotaxanes: correlation of photophysics and nature of encapsulations*, *Eur. Phys. J. Appl. Phys.*, accepted October 2016

## B. Book chapters

1. A. Farcas, P.-H. Aubert; Electrochemical studies of conjugated polyrotaxanes and their unthreaded analogues; (invited chapter); Encyclopedia of Physical Organic Chemistry ed. by Wang Zerong, John Wiley & Sons Inc; Hardcover–February (2017); <https://www.amazon.co.uk/Encyclopedia-Physical-Organic-Chemistry-Zerong/dp/1118470451>
2. A. Farcas, A.-M. Resmerita; Supramolecular chemistry: synthesis and photophysical characteristics of conjugated polyrotaxanes; (invited chapter); Encyclopedia of Physical Organic Chemistry ed. by Wang Zerong, John Wiley & Sons Inc; Hardcover–February (2017); <https://www.amazon.co.uk/Encyclopedia-Physical-Organic-Chemistry-Zerong/dp/1118470451>

### C. International conferences

1. A. Farcas, A.-M. Resmerita, F. Farcas, Terpolymer polyrotaxanes: a promising supramolecular system as electron-transporting materials for optoelectronics, The 8th edition of the International Conference "Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies", ATOM-N 2016, 25 - 28 august 2016, Constanta, Romania
2. A. Farcas, A.- M. Resmerita, P.- H. Aubert, Conjugated polyrotaxanes: a critical assessment of photophysical properties in correlation with the effect of the nature of host molecules encapsulation, Nanotech France 2016, International Conference and Exhibition, 01-03 IUNIE 2016, Paris - France
3. A.-M. Resmerita, F. Farcas, A. Rotaru, A. Farcas, Synthesis and photophysics of conjugated azomethine polyrotaxanes, The 8th edition of the International Conference "Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies", ATOM-N 2016, 25 - 28 august 2016, Constanta, Romania

### D. Best paper award

1. A. Farcas, "Terpolymer polyrotaxanes: a promising supramolecular system as electron-transporting materials for optoelectronics", The 8th edition of the International Conference "Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies", ATOM-N 2016, 25 - 28 august 2016, Constanta, Romania